



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : KUTSUNA, Takaaki, et al.

Serial No. : 10/015,564 (parent)

Filed : December 17, 2001

For : COMPOSITION FOR COATING HAVING A GAS  
BARRIER PROPERTY, COATING AND COATED  
FILM HAVING A GAS BARRIER POROPERTY USED  
THE SAME

D E C L A R A T I O N

Honorable Commissioner of

Patent & Trademarks

Washington, D.C. 20231

I, Shuta KIHARA, Japanese citizen, residing at c/o  
Mitsubishi Gas Chemical Company Inc., Hiratsuka Research  
Laboratory 6-2, Higashiyawata, 5-chome, Hiratsuka-shi,  
Kanagawa, Japan,

Declare:

That I am an inventor of the above application, and  
familiar with the invention and prosecution history of said  
application ;

I performed the following experiments to

demonstrate that the composition for coating of the present invention exhibits more excellent gas barrier property than a composition for coating containing components of an epoxy resin and the curing agent for epoxy resin comprising polyamine compound (A) and fatty amine compound (B) disclosed in Japanese Patent Publication No.8-104738.

### Experiments

#### Example 3

Oxygen permeation factor and oxygen permeability for the coated film obtained in Example 3 were again evaluated. The oxygen permeation factor was 0.033 (cc-mm/m<sup>2</sup> · day · atm) and the oxygen permeability (thickness 4 μ m) was 8.3 (cc/m<sup>2</sup> · day · atm).

#### Comparative Example 9

8 parts by weight of octadecylamine (FARMIN 80, manufactured by Kao Co, Ltd, in Japan) was mixed with 100 parts by weight of amine curing agent C and a mixture thus obtained was maintained to a uniform state with heating and cooled to a room temperature, whereby amine curing agent C' was prepared.

A MFG solution containing 57 parts by weight of amine curing agent C' and 50 parts by weight of an epoxy resin with tetraglycidylamine moiety derived from metaxylylenediamine, manufactured by Mitsubishi Gas Chemical

Co., Inc., TETRAD-X was prepared and 0.02 parts by weight of an acrylic wetting agent, manufactured by BYK · Chemi GmbH, BYK381 was added thereto and stirring was sufficiently performed, whereby a coating solution was prepared. The coating solution thus obtained was coated on a base material (polyethylene terephthalate film, 100  $\mu$  m) and curing reaction was performed at 60°C for one hour and then further at 120°C for 30 minutes, whereby a coated film was prepared on the base material. Oxygen permeation factor and oxygen permeability for the coated film thus obtained were evaluated. The oxygen permeation factor was 0.456 (cc-mm/m<sup>2</sup> · day · atm) and the oxygen permeability (thickness 4  $\mu$  m) was 114 (cc/m<sup>2</sup> · day · atm).

#### Conclusion

In comparison between Example 3 and Comparative Example 9, the composition for coating of the present invention exhibits more excellent gas barrier property than that disclosed in Japanese Patent Publication No.8-104738.

The undersigned declarant declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this day of July 12, 2006

Shuta Kihara

Shuta KIHARA



### DECLARATION

I, Tadashi YAMAMOTO, a national of Japan, c/o Yamamoto International Patent Office of 520 Sanno Urbanlife, 1-8, Sanno 2-chome, Oota-ku, Tokyo 143-0023, Japan do hereby solemnly and sincerely declare:-

- 1) THAT I am well acquainted with both Japanese Language and English language, and
- 2) THAT the attached document is a full, true and faithful partial translation into English made by me of Japanese Patent Publication No. 47-30640B

The undersigned declarant declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Singed this day of October 12, 2006.

Tadashi YAMAMOTO

Partial English translation of Japanese Patent Publication

Patent Publication No. 47-30640

Patent Publication date: August 9, 1972

Patent Application No. 42-25137

Application date: April 21, 1967


Inventor(s): Tomohiko Asahara, et al

Applicant: Toray Co, Ltd.

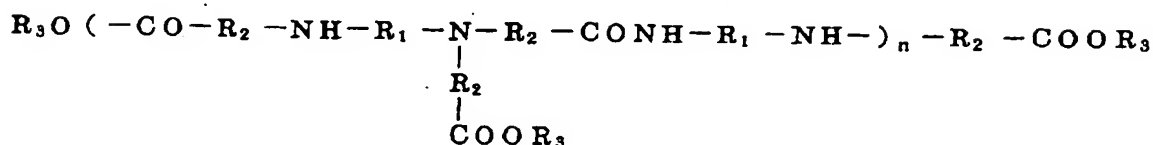
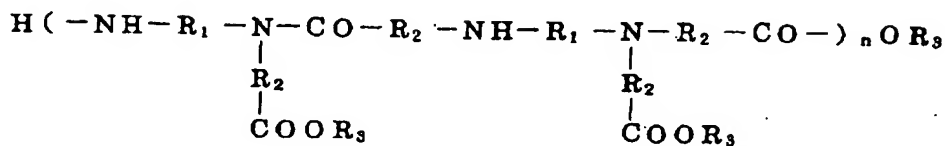
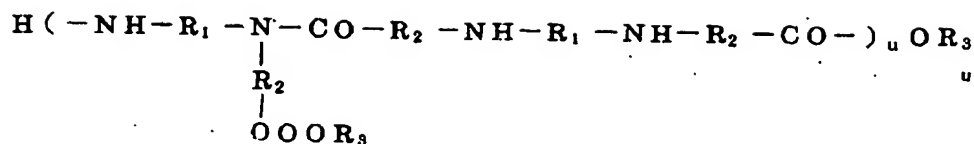
Title of the invention: Process for producing a thermosetting resin with heat resistance

(Names of individuals and corporation have been translated phonetically)

(Page 1, col.2, lines 6 to page 2, col.4, line 36)

The invention is a process for producing a thermosetting resin with heat resistance which comprises adding an uncured epoxy resin to an amide-amine oligomer having amide bond in its main chain and branching of  $-R_2-COOR_3$  ( $R_2: -CH_2CH_2-$  or  $-CH_2CH_2-$  ,  $R_3$ : a hydrocarbon-yl group) bonded to nitrogen of the amide group obtained by an aromatic diamine and excess mol of acrylate or p-vinylbenzoate to the aromatic diamine and heating.

The amide-amine oligomer to be used for the production of the thermosetting resin with heat resistance can be obtained by reaction of the above-mentioned starting materials. Examples of the amide-amine oligomer thus obtained include oligomers of the following compounds or a mixture unit thereof.



R<sub>1</sub>: aromatic hydrocarbon-diyl group



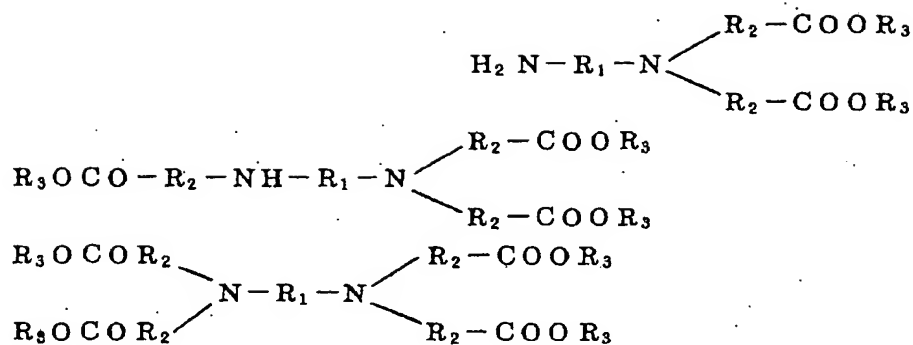
R<sub>2</sub>: --CH<sub>2</sub>CH<sub>2</sub>-- or --CH<sub>2</sub>CH<sub>2</sub>

R<sub>3</sub>: hydrocarbon-yl group

These hydrocarbons may be substituted by an inactive organic residue group.

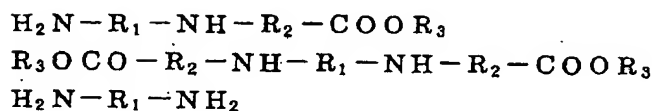
The amide-amine oligomer is not a polymer, because a polymer thereof requires its considerable amount for cure of an epoxy resin, so that there is a danger to impair equality as an epoxy resin, though there is no hindrance for curing reaction per se, and furthermore there is difficulty in operation for mixing with an epoxy. The molecular weight of the oligomer is preferably about 200 to 2000.

In more detail, a process for producing the amide-amine oligomer, for example, comprises reacting 1 mol of an aromatic diamine with more amount than 1 mol of an acrylate or an p-vinylbenzoate to produce amino acid esters with the following branched structures and then mixing at least on species thereof and heating, thereby obtaining an amide-amine oligomer.]



(R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are defined above)

Further, the amino acid ester with the above mentioned structures may be mixed with the following amine or amino acid ester.



(R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are defined above)

The feature of the amide-amine oligomer constituting the thermosetting resin with heat resistance of the invention is in that it has primary amino group or an ester group on its end and has secondary amino group or tertiary amino group with lower reactivity than the primary amino group in its molecule. That is, since the reactivity of primary amino group or ester group is higher than that of secondary amino group, polycondensation reaction due to primary amino group or



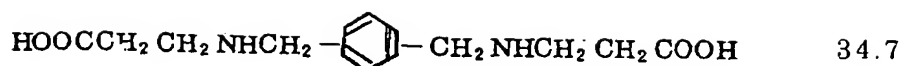
ester group proceeds dominantly. Therefore, thermally stable polyamide chain is sufficiently formed. On the other hand, since cross-linking due to secondary amino group proceeds in a small amount, a thermosetting resin with excellent flexibility is formed.

(Page 4, col. 8, lines 28 to page 5, col. 9, line 25)

#### Example 1

12.90g (0.150mol) of methyl acrylate dissolved in 15cc of methanol was dropwise added to 1360g (0.100mol) of metaxylylenediamine maintained at 80°C with intense stirring within 2 hours. The reaction was performed for further 4 hours and then heating was performed under a reduced pressure of 400 mmHg for 3.5 hours at 140°C. An amide-amine oligomer thus obtained had an average molecular weight of 633. An automatic analysis of amino acid was conducted for the product obtained by hydrolysis of its portion with hydrochloric acid. It was found that the following various amino acids are present in the following molar ratio:

|  | mol% |
|--|------|
| $\text{H}_2\text{NCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{N}\begin{cases} \text{CH}_2\text{CH}_2\text{COOH} \\ \text{CH}_2\text{CH}_2\text{COOH} \end{cases}$                  | 8.1  |
| $\text{HOOCCH}_2\text{CH}_2\text{NHCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{N}\begin{cases} \text{CH}_2\text{CH}_2\text{COOH} \\ \text{CH}_2\text{CH}_2\text{COOH} \end{cases}$ | 16.4 |
| $\text{H}_2\text{NCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{COOH}$   | 31.6 |



Others

about 10%

Thus, the amide-amine oligomer is an oligomer with a branched structure. The amide-amine oligomer and an epoxy resin prepolymer Epikote 828 (manufactured by Shell Co.,) were mixed in a ratio of 6/1 and maintained under 80°C/30mmHg for about 2 hours and then maintained at 130°C for 20 hours, at 150°C for 5 hours, at 170°C for 3 hours and at 190 to 200°C for 2.5 hours. The product thus obtained a sirup-colored transparent solid having no flowability and caused no foaming.

A thermal weight analysis (a temperature raising rate of 6°C/mm) was performed for the product in a flowing air of 200cc/min. It was found that it is a cured product with good heat resistance having 10% reduced weight point. It was pulverized with a ball mill. An infrared spectrum was measured. Since the magnitude of estercarbonyl absorbance is about 6 to 8% to that of amide (a ratio of ester absorbance / amide absorbance of the amide-amine oligomer prior to curing: about 2/5), it is confirmed that polycondensation proceeds in the system.

(Page 8, col., 15, line 4 from the last to col. 16, line 6 from the last)

Claim:

1. A process for producing a thermosetting resin with heat resistance which comprises adding an uncured epoxy resin to an amide-amine oligomer having amide bond in its main chain and branching of  $-\text{R}_2-\text{COOR}_3$  ( $\text{R}_2: -\text{CH}_2\text{CH}_2-$  or  $-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-$ ,  $\text{R}_3$ : a hydrocarbonyl-yl group) bonded to nitrogen of the amide group obtained

by an aromatic diamine and excess mol of acrylate or p-vinylbenzoate to the aromatic diamine and heating.